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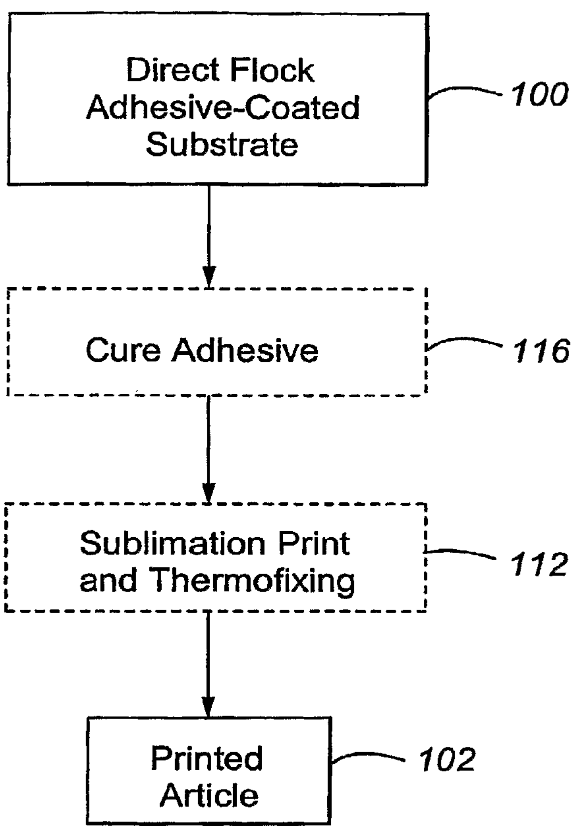
(54) Title: PROCESS FOR HIGH AND MEDIUM ENERGY DYE PRINTING A FLOCKED ARTICLE



(57) Abstract: The processes and articles of the present invention use thermally stable and loft retentive polymers in sublimation printed flock fibers, which are particularly attractive for forming molded and heat laminated articles. The process and articles use high, medium and low energy dyes on the fibers. A preferred polymer for use in the fibers is poly(cyclohexylene-dimethylene terephthalate).

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PROCESS FOR HIGH AND MEDIUM ENERGY DYE PRINTING A FLOCKED ARTICLE

FIELD OF THE INVENTION

The present invention is related generally to printing of flocked articles and specifically to sublimation ink printing of flocked articles.

BACKGROUND OF THE INVENTION

Flock is used in the manufacture of numerous types of articles, such as textiles. Such articles are typically manufactured by electrostatically depositing the flock onto the desired surface. In one process, the desired surface is a release-adhesive coated sacrificial carrier sheet. The free ends of the flock are then contacted with an adhesive. This structure, also known as a transfer, is thermally applied to the substrate. In another process, the desired surface is a permanent adhesive or the substrate itself. This process is known as direct flocking. The direct flocked structure generally does not include a carrier sheet and release adhesive.

Flock fibers may be either pre-dyed (before application to the desired surface) or post-dyed (after application to the surface). Post-dyeing may typically be effected by sublimation dyeing techniques in which the flock and dye are heated so that the vaporized dye is transferred to the flock fiber. A sublimation print in the desired design typically carries the dye for transfer to the flock either by direct print (e.g., screen or inkjet) or heat transfer techniques. As used herein, "sublimation" refers to a process where an image is printed by turning dye, ink or toner by heat and/or pressure and/or dwell time into a gas which then impregnates itself into a substrate or a coating on a substrate, typically by thermofixing.

The use of sublimation ink printing of flock has generally not been widely practiced because it has produced a very low quality product. Some polyester flock fibers, such as poly(ethylene terephthalate), can hold the dye but have a low deformation temperature, little loft retention, poor shape memory and flatten out during sublimation ink printing and are not heat-settable or soft. Other polyester flock fibers typically melt or soften and deform under the high temperatures experienced during sublimation ink printing, losing desirable tactile characteristics (soft touch and plushness). Nylon and rayon flock fibers, though having loft retention, generally are unable to accept the vaporized dye consistently and/or permanently and therefore produce an irregular and/or unstable colored product and offer designers a limited color palette.

SUMMARY OF THE INVENTION

These and other needs are addressed by the various embodiments and configurations of the present invention. The processes and articles of the present invention use a variety of dye particle types in thermally stable and loft retentive sublimation printed flock fibers, which are highly attractive for molded resin articles and for textiles, including upholstery and carpet.

The dye particles can be any type of coloring agent, with latent dyes such as direct dyes, fiber-reactive dyes, solvent dyes, acid dyes, leuco dyes, natural and synthetic dyes, and disperse dyes being preferred. A direct dye is a water-soluble dye taken up directly by fibers from an aqueous solution containing an electrolyte, presumably due to selective adsorption. A fiber-reactive dye is a synthetic dye containing reactive groups capable of forming covalent linkages with certain portions of molecules of natural or synthetic fibers. A solvent dye is an organosoluble dye. A natural dye is an organic colorant obtained from an animal or plant source. A synthetic dye is an organic colorant derived from coal-tar- and petroleum-based intermediates. Disperse dyes are a group of non-ionic dyes with no water soluble groups in their structures and are applied at a high temperature. Chemical classes of disperse dyes include azo, nitroarylamine, and anthraquinone. Disperse dyes commonly contain amino or substituted amino groups but no solubilizing sulfonic groups. They are commonly water-insoluble dyes introduced as a dispersion or colloidal suspension in water and are absorbed by the flock fiber. Dyes, particularly disperse dyes may, be divided into three types, specifically high energy, medium energy, and low energy according to their application properties. Each type of disperse dye molecule exhibits different particle size-and-dispersability-to-temperature relationships.

The dye particle types used in the present invention include not only low energy dye particles but also high and medium energy dye particles. Low, medium, and high energy dyes commonly have differing atomic/molecules sizes and require relatively high transfer temperatures, typically at least about 200 degrees Celsius, and more typically at least about 204 degrees Celsius, and as a result can offer excellent permanence and wash-fastness. Although low energy dye particles have been employed for polyester flock fibers, medium and high energy dyes have generally required a greater degree of thermal stability of the fibers than polyester flock fibers have heretofore offered.

The flock fibers may be any sublimation printable material, which typically is composed primarily of a thermally stable polymer. Examples of thermally stable

polymers include crystalline polyesters, poly(phenylene sulfide) or PPS, a liquid crystal polymer or LCP, a high temperature polyamide, and blends thereof. More preferably, the flock fibers are composed primarily of poly(cyclohexylene-dimethylene terephthalate) ("PCT"), copolymers include poly(ethylene terephthalate co-1,4-cyclohexylene dimethylene terephthalate), co-polyesters including PCTA™ manufactured by Eastman Chemical Company, polyesters including poly(1,3 propylene terephthalate) which is also called poly trimethylene terephthalate (PTT) or Corterra™, copolymers of cyclohexylene-dimethylene terephthalate and ethylene terephthalate, polyethylene terephthalate, and blends thereof. The flock fibers may be bicomponent fibers as discussed in U.S. Provisional Patent Application Serial No. 11/036,887, filed January 14, 2005, which is incorporated herein by this reference. The flock fibers can be of any suitable denier or dimensions, with flock being preferred, and can be used for a wide range of applications, including printed flocked articles, carpet, and the like. Particularly preferred applications include nonwoven articles in which the flock fibers are adhered to a substrate and are free-standing. In one application, the fibers are flock and are at least substantially perpendicular or normal to the substrate.

The dye may be applied to the printable flock with or without a carrier. The carrier may include one or more meltable or sublimable materials that form a vapor or liquid to assist in transporting the dye particles or molecules from the printed layer to the fibers. The carrier may include dying assistants to assist in color development on the fibers. Typically, the flocking material is a white, clear or slightly opaque polyester or other synthetic fiber and may contain a dye or pigment such as titanium dioxide. A suitable dye or pigment is applied to the flock to cause dyeing or coloration of the flock after application to the underlying (or overlying) layer (depending on the order in which the various layers are deposited). The dyes or pigments include transfer and direct printing sublimation inks containing low, medium and high energy dyes (as noted above), acid dye inks, and pigment dyes. As will be appreciated, dye sublimation refers to a process in which specially formulated inks vaporize when heated and bond with the molecules of the material to which they are being transferred. Dye sublimination is the preferred technique to provide desired color patterns to the design (e.g., flock fiber substrate) due to the superior feel of the design. Sublimation ink transfer printing is preferred over sublimation direct printing for reasons of cost and throughput, the ability to produce certain quality graphics and portability, the lack of added "hand" or ink body, the cleanness of the process, and minimal set up. As will be appreciated, sublimation ink

direct printing, unlike sublimation ink transfer printing, may be more likely to leave excess dye on the surface texture of fibers that must be washed out after printing and requires post-printing heat curing to locate the dye in the fiber. The colored fibers in the design can have as soft or softer feel than fibers colored using other printing techniques or of other compositions. A softer feel is more attractive to consumers in many applications. The dye is more colorfast in the flock fiber as the dye is absorbed at high temperature and fixed by the fiber as opposed to simply being a surface coat on the fiber. Unlike sublimation dyes, non-sublimation dyes, such as acid dye inks, generally must be cured after application, such as by steam curing (which can be impractical and cumbersome).

The flock of the present invention, when combined with the various flocking techniques set forth herein, can provide a wide format design inexpensively and in high volumes, particularly using sublimation ink transfer printing. Unlike certain other polyesters, the flock of the present invention can withstand the high temperatures and pressures used during sublimation transfer printing while maintaining the loft, flexibility, resilience, and plush appearance of the fibers. Typically, the shrinkage experienced by the flock fibers during sublimation ink printing, including heat lamination or sublimation transfer printing, is no more than about 5% and even more typically is no more than about 2.5% in length. Such designs are particularly attractive when combined with highly resilient flock such as thermally modified PCT. When compared to PET flock fibers, PCT flock fibers shrink much less, are able to withstand higher temperatures without deforming, and can tolerate a higher thermofixing temperature range due to PCT's higher deformation and/or melting temperature. Due to high wear/abrasion resistance, thinness, and color fastness of the printed articles of certain embodiments of the present invention, the printed articles of the present invention are useful for a wide variety of applications, including application to automotive interiors, cellular telephone covers, computer key pad and other touch surfaces, membrane-type molded films, and the like. PCT, being a type of polyester, can adhere well to many coatings and finishes that non-polyester fibers, such as nylon, are not capable of permanently adhering for prolonged periods. For example, PCT is able to accept stain-resistant coatings such as Scotchgard™ and can accept a softening finish.

These and other advantages will be apparent from the disclosure of the invention(s) contained herein.

As used herein, "vinyls" refer to a compound including the vinyl grouping (CH2=CH-) or a derivative thereof; "urethanes" to a compound including the grouping

$CO(NH_2)OC_2H_5$ or a derivative thereof; nylons to a compound having the grouping -CONH or a derivative thereof; acrylics to a compound including the acrylonitrile grouping or a derivative thereof; acetates to an ester of acetic acid where the substitution is by a radical; olefins to a class of unsaturated aliphatic hydrocarbons having one or more double bonds; and amides to a class of compounds comprising an acyl group (-$CONH_2$) typically attached to an organic group "R", where R can include hydrogen, an alkyl group, and an aryl group.

As used herein, " at least one", "one or more", and "and/or" are open-ended expressions that are both conjunctive and disjunctive in operation. For example, each of the expressions "at least one of A, B and C", "at least one of A, B, or C", "one or more of A, B, and C", "one or more of A, B, or C" and "A, B, and/or C" means A alone, B alone, C alone, A and B together, A and C together, B and C together, or A, B and C together.

The above-described embodiments and configurations are neither complete nor exhaustive. As will be appreciated, other embodiments of the invention are possible utilizing, alone or in combination, one or more of the features set forth above or described in detail below.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a first process embodiment according to the present invention;

Fig. 2 is a first flocked article embodiment made by the process of Fig. 1;

Fig. 3 is a second process embodiment according to the present invention;

Fig. 4 is a second flocked article embodiment made by the process of Fig. 3;

Fig. 5 is a fourth process embodiment according to the present invention;

Fig. 6 is a fourth flocked article embodiment made by the process of Fig. 5;

Fig. 7 is a third process embodiment according to the present invention;

Fig. 8 is a third flocked article embodiment made by the process of Fig. 7;

Fig. 9 is a third flocked article embodiment made by the process of Fig. 7;

Fig. 10 is a third flocked article embodiment made by the process of Fig. 7;

Fig. 11 is a seventh process embodiment according to the present invention;

Fig. 12 is a seventh flocked article embodiment made by the process of Fig. 11;

Fig. 13 is a seventh flocked article embodiment made by the process of Fig. 11;

Fig. 14A is a fifth process embodiment according to the present invention;

Fig. 14B is a fifth flocked article embodiment made by the process of Fig. 14A;

Fig. 15 depicts the chemical formula of a family of polymers including PCT;

Fig. 16 is a sixth process embodiment according to the present invention;

Fig. 17 is a sixth flocked article embodiment made by the process of Fig. 16;

Fig. 18 is a sixth flocked article embodiment made by the process of Fig. 16;

Fig. 19 is a sixth flocked article embodiment made by the process of Fig. 16;

Fig. 20 is a sixth flocked article embodiment made by the process of Fig. 16;

Fig. 21 is a sixth flocked article embodiment made by the process of Fig. 16;

Fig. 22 is a plot of length (microns) (vertical axis) against temperature (degrees Celsius) for various polymer fibers;

Fig. 23 depicts the chemical formula of a family of polymers including PTT;

Fig. 24 is a plot of length (microns) (vertical axis) against temperature (degrees Celsius) for various polymer fibers;

Fig. 26 depicts the reactions during silicone adhesive curing according to an embodiment of the present invention; and

Fig. 27 depicts the adhesion mechanism of silicone adhesives to paper.

DETAILED DESCRIPTION

Sublimation Printed Articles

The various embodiments of the present invention utilize a thermally stable polymer, copolymer, or polymer blend with loft retention as the flocking fiber. Sublimation ink printing typically heats and applies pressure to the flocked article to permit dye to be transferred and heat set via the vapor phase from a temporary carrier substrate to the fiber. Many polyester flock fibers, such as polyethylene terephthalate, deform at such temperatures/pressures and/or have poor loft retention, because of the temperature and pressure required for sublimation dye to sublime, thereby causing an unattractive article and unpleasant surface to the touch and loss of orientation (which detrimentally impacts the tactile sensation or experience of softness). Some fibers do not accept dyes relatively permanently, such as polyamide fibers (e.g., various types of nylons) and cellulose fibers (e.g., rayon).

The polymers, copolymers, and polymer blends of the present invention can overcome these limitations. For sublimation ink transfer printing, the heat set polymers, copolymers, and polymer blends preferably have a melting point, deformation temperature, and softening point that are greater than and more preferably at least about 5 degrees greater than the temperature to which the flock will be heated during sublimation ink printing (and, if applicable, molding). This temperature is typically at least about

340°F, more typically at least about 410°F, and even more typically ranges from about 415°F to about 450°F. The polymers, copolymers and polymer blends preferably will accept dye, and are highly flexible and elastic with a high degree of shape memory (*e.g.*, high percentage of shape recovery after compression). These features preferably are maintained despite the temperatures and/or pressures experienced during sublimation ink transfer or direct print thermofixing. The pressures experienced during sublimation ink transfer printing typically are at least about 2 psi, and even more typically range from about 2 psi to about 30 psi.

In one embodiment, the flock comprises a polyester having one or more terephthalate groups and preferably the repeating unit formula set forth in Figure 15. With reference to that figure, "R" represents independently hydrogen or a substituted or unsubstituted alkyl or aryl group and "S" is an aromatic or nonaromatic cyclic residue which can include one or more heteroatoms. In a particularly preferred embodiment, the flock comprises the polyester poly(cyclohexylene-dimethylene terephthalate) ("PCT"), with poly(1,4-cyclohexylene-dimethylene terephthalate) being preferred and PCT polyester, such as Thermx™ or Thermx EG™, from Eastman Chemical Company being even more preferred. As will be appreciated, the polyester shown may be modified to make a co-polyester by substituting some or all of the terephthalate with isophthalate (known as PCTA) or another diester and/or substituting some or all of the cyclohexane dimethanol with another diol.

To provide greatest or optimal thermal stability, the polymer should be crystallized but have substantial amorphous (uncrystallized) regions. Typically, the polymer in the fiber is at least about 15% and more typically at least about 50 to 80% crystalline% and at least about 50% and more typically at least about 20% amorphous. Even more typically, the polymer is from about 50% to about 80% crystallized, preferably the heat set temperature is/are at least as high or preferably higher than the maximum temperature experienced by the fiber in later processing, such as sublimation ink printing or thermofixing. More preferably, the temperature is at least about 180°C, more preferably at least about 190°C, and even more preferably at least about 200°C. The temperature is preferably no more than about 300°C. This temperature can be important to providing PCT with suitable properties for sublimation ink printing to "lock in" the resiliency or provide heat resistance and stability. As will be appreciated, during heat setting some crystalline regions in the polymer form and grow, making the polymer thermally stable. If the polymer is later heated to a temperature at or above the heat set

temperature, these crystalline regions will remelt, thereby adversely impacting the physical properties of the polymer. It is important not to draw the polymer too much to inhibit or restrict the formation and growth of the crystalline regions or at too high a temperature to overly crystallize the polymer. Typically, the polymer is drawn from about 110 to about 500% of its original length during the drawing step at a fiber temperature above the glass transition temperature and below the melting point of the fiber. As will be further appreciated, additives can be added to the PCT, as in the case of ThermxA™ or PCTA™, to change the deformation and melting temperatures. As will be appreciated, other diacids and/or diols can be substituted in the PCT polymerization to make co-polyesters, as in the case of PCTA™.

Additionally, the fibers can be singed, calendared, or embossed.

The preferred polymer composition comprises at least about 25 wt.% PCT, more preferably at least about 50 wt.% PCT, and even more preferably at least about 75 wt.% PCT. The composition may include other desirable additives, typically at least about 0.1 wt% and more typically from about 0.5 to about 25 wt% plasticizer(s). Suitable plasticizers are known to those skilled in the art.

The superior properties of PCT are also amenable to flock coloration using low, medium, and/or high energy sublimation dyes in ink formulations. As will be appreciated, flock can be colored by sublimation inks by many techniques, including sublimation ink direct or heat transfer ink printing. In such coloration techniques, the flocking material is a white or natural flock and a sublimation dye is added to the white flock by suitable techniques after flock application to the underlying (or overlying) adjacent adhesive layer (which may be located on a carrier).

To accept the dye effectively, the polymer in the flock fiber preferably has polar functional groups (such as polyesters) and comprises no more than about 5 wt.% and even more preferably no more than about 1 wt.% pigments, such as titanium dioxide, and the flock fiber has sufficient aspect ratio (ratio of diameter to length) to effectively withstand the thermal demands of sublimation ink printing and accept the dye. Preferably, the fibers have a diameter of at least about 1 denier and more typically ranging from about 2 to about 50 denier and a length of from about 0.5 to about 2mm.

In the various sublimation ink printing or thermofixing techniques, the sublimation dye is heated until the dye enters the vapor phase (by direct conversion of the solid phase to the vapor phase). The flock fibers are also heated to about the same temperature as the vaporized dye. When the flock fibers are heated above the glass

transition temperature of the component polymer, the intermolecular distance in the amorphous regions of the fiber increases due to the effects of thermal energy. The dye atoms/molecules enter into the intermolecular spaces in the amorphous regions, or the flock fiber accepts the vaporized dye, which colors the flock fibers. As will be appreciated, the molecular sizes of the dye molecules increases in direct relationship with the energy of the dye, with high energy dyes having larger molecular sizes than medium and low energy dyes and medium energy dyes than low energy dyes. The differences in molecular sizes causes high energy dyes to require more thermal energy than medium and low energy dyes and medium energy dyes more thermal energy than low energy dyes to sublime and migrate to the flock fibers due at least in part to attraction to the polymer's polar groups. During dye application and, depending on the sublimation ink printing or thermofixing technique, subsequent thermofixing under heat, temperatures (typically of at least about 340°F and more typically ranging from about 350°F to about 440°F generally or at least about 390°F and more typically ranging from about 400 to about 410°F for low energy dyes, at least about 410°F and more typically ranging from about 420 to about 430°F for medium energy dyes, and at least about 420°F and more typically ranging from about 430 to about 500°F for high energy dyes) and pressure (typically of at least about 2 psi and more typically ranging from about 12 to about 50 psi) is/are applied to the flock and can flatten or deform flock fibers. To resist the pressure applied during sublimation transfer printing, it is preferred that the polymer have a deformation temperature at least as high as the maximum temperature experienced by the polymer flock fiber during sublimation ink printing/pressure application. When the fiber is cooled to below the glass transition temperature, the dye atoms are trapped in the molecular structure of the polymer.

The PCT-containing flock can be applied by electrostatic, gravity, air flow, and vibrating techniques directly to a substrate or to a temporary carrier for indirect application to the substrate.

In one configuration, the adhesive contacting the fixed ends of the flock is colored, either before or after sublimation printing of the flock fibers, in a pattern matching the pattern imparted to the flock during sublimation printing. In this manner, wear patterns to the flocked surface which dislodges flock fibers are less visible. The adhesive may be a film that is colored before sublimation printing, such as by including dye, pigment particles, or other colorants in the resin during film manufacture. This approach is particularly attractive for single color flock designs. Multi-color patterns

could be difficult to pre-color using this approach due to misalignment or misregistration between the pattern on the adhesive and the pattern imparted to the flock during sublimation printing. For multi-color patterns, the adhesive is preferably colored during sublimation printing simultaneous with and by the same sublimation inks used to color the flock fibers. To make this possible, the adhesive is typically selected to accept the low, medium, or high energy dye at least about 50% as well, more typically at least about 75% as well, and even more typically at least as well as the flock fibers. The adhesives may also be colored by a pigment. Preferred adhesives include thermoplastic or thermosetting polyester adhesives, co-polyesters, polycarbonates, acrylic adhesives, cyano acrylate adhesives, isocyanate-containing adhesives, epoxy adhesives, and one- and two-part thermoset adhesives, and mixtures, blends, and copolymers thereof. Particularly preferred adhesives are cross-linkable thermosetting adhesives, such as polyurethane adhesives. The preferred adhesive can be a solvent adhesive such as isocyanate catalyzed adhesives or a pre-formed film adhesives, such as a polyurethane film. To sublimation print the adhesive, the adhesive and flock must each be brought to a temperature high enough to effect transfer of the dye to and "molecular entrapment" acceptance of the dye by both the flock and the adhesive.

The flock fibers and manufacturing techniques of the present invention can provide a printed article having a high degree of plushness. A "plush flock fiber texture" is commonly not simply a matter of longer flock fiber length. Theoretically, a very long flock fiber coating could still not be "plush" if the fibers are disoriented, density low, etc. A plush flock fiber texture has a high degree of resilience or "tactile sensation" or dimension (or "loft") of the fiber coating. Plushness is typically a combination of the following qualities or physical properties:

- fiber type (durometer, softness or hardness of the plastic, resilience of the fiber itself);
- fiber diameter (denier or decitex);
- fiber density (grams per square meter);
- fiber cut length (mm or thousandths of an inch);
- even-ness of the cut (unevenly cut fibers, flocked together, actually can feel softer than uniform cut length);
- depth into the adhesive the fibers are planted or situated;
- angle of fibers in the adhesive;
- uniformity of angle of fibers in adhesive—all going in same direction or in

diverse directions;

- softness of the adhesive base resin and/or if it's been foamed (softer) with air; and
- even-ness of adhesive coating: thicker or thinner in areas.

After thermosetting, at least most of the fibers preferably have a fiber diameter of from about 0.3 to about 75 denier, have a fiber density ranging from about 40% to about 80%, have a fiber cut length ranging from about 0.5 to about 2 mm and even more preferably from about 1 to about 1.5 mm, are relatively evenly cut, have a depth of implantation in the permanent adhesive of no more than about 3% of the fiber length, and have an angle of implantation that is substantially perpendicular to the plane of the adhesive layer. The permanent adhesive is preferably relatively soft and evenly applied over the fibers and has a thickness ranging of from about 1 to about 5 microns (which depends on the fiber length).

Plushness can be important. The "experience of softness" is sometimes defined as resistance or lack of resistance to the touch or to a force—the ability (or resistance to) bending, yielding, and also can relate to slipping (longitudinal movement along a fiber with lack of resistance—easy slipping can make a soft fiber feel "wet"). With rich texture, plushness, "body", the perceived value of a wide range of products can be affected—and therefore peoples' willingness to buy them increases.

The Process and Article of the First Embodiment

Referring to Figures 1 and 2, the process and article of the first embodiment of the present invention will now be described.

In the first step 100, the adhesive-coated substrate 104 is direct flocked by known techniques using the flock of the present invention. The PCT-containing flock is typically white in color or contains little pigment and can be flocked by any suitable technique, with electrostatic flocking being preferred. The adhesive may be applied discontinuously to the substrate in a desired (direct) image.

The adhesive used in adhesive layer 108 may be any suitable permanent adhesive (as opposed to a release adhesive) that is thermally compatible with the sublimation ink printing temperature used in step 112. "Thermal compatibility" depends on the process configuration. When the adhesive is cured (*e.g.,* fully activated, set, cross-linked, fused, otherwise fully bonded) 116 before sublimation ink printing in step 112, thermal compatibility is deemed to exist when the adhesive integrity will not be detrimentally impacted by the later sublimation ink printing temperature, such as by softening,

tackifying, melting, or matting down the fibers. When the adhesive is cured during or simultaneously with sublimation ink printing, thermal compatibility is deemed to exist when the temperature required to fully activate, set, cross-link, fuse, or otherwise fully bond the adhesive is at or below the sublimation ink printing temperature. When the adhesive is cured after sublimation ink printing, thermal compatibility is deemed to exist when the temperature required to fully activate, set, cross-link, fuse, or otherwise fully bond the adhesive is above the sublimation ink printing temperature.

Preferred adhesives can be any suitable adhesive, with water- and solvent-based adhesives and solid being preferred. Particularly preferred adhesives include thermoset and hot melt thermoplastic adhesives. As will be appreciated, thermoset adhesives solidify, activate and/or set irreversibly when heated above a certain activation temperature. This property is usually associated with a cross-linking reaction of the molecular constituents induced by heat or radiation. Thermoset adhesives can include curing agents such as organic peroxides, isocyanates, or sulfur. Examples of thermosetting adhesives include polyethylene, phenolics, alkyds, amino resins, polyesters, epoxides, polyurethanes, polyamides, and silicones.

Following curing of the adhesive layer 108 in step 116 (or 112), which is typically performed using radiation (*e.g.*, heat or light) the flocked surface can be vacuumed and vibrated to dislodge and remove loose flock fibers. This removal of loose flock fibers can improve the quality of the image in the later sublimation ink printing step and eliminate the chance for contamination.

In sublimation ink printing step 112, the flocked surface 120 is sublimation printed and the dye particles thermofixed in the fibers by any suitable technique to provide multi-colored flock in a desired design. As noted, common ways of performing sublimation ink direct printing include inkjet or screen sublimation ink printing and sublimation transfer printing (e.g., using a transfer carrier) using devices such as an inkjet dye sub printer, a ribbon-based dye sub printer, a hybrid sublimation printer, and a small dye sub ribbon-based printer. Other printing techniques include offset printing, flexo printing, gravure printing, rotary screen printing, etc.

In inkjet (direct) sublimation ink printing, a special heat sensitive dye is used in a computer-controlled printer, such as an HP 550™, or Mimaki JV4™ to print sublimation ink onto the flock fibers through direct deposit of the ink from the printer to the flock fibers. The printed dye is then heat and pressure thermofixed and thereby enters the amorphous areas of the flock fiber matrix.

In sublimation heat transfer ink printing, special heat sensitive dye is firstly deposited on a carrier paper or film. The paper or transfer is printed by a suitable technique, such as offset printing, screen printing, rotograviere printing, heliographic or flexographic printing or serigraphic printing by flat plate or rotary plate to deposit dye onto a carrier and then dried. Transferring is done by placing the transfer in contact, under regulated pressure and at a predetermined temperature and dwell time, generally with the aid of hot rolls or drums, platens with the flocked surface, generally for a duration of about 5 seconds to about 1 minute. The hot drums can comprise, in the case of printing in formats, a hot press with horizontal platens, or in the case of continuous printing from rolls of printed paper and of synthetic material to be printed, a rotating heated cylinder associated with a belt rolling under tension.

Surprisingly and unexpectedly, flock fibers 120 of the present invention, after experiencing the pressures and temperatures of sublimation ink printing, maintain their printing orientations and original form (not deformed). This loft retention may be improved by vacuuming the dyed flock fibers after rather than before sublimation ink printing. The retained orientation of at least most of the flock fibers is, as shown in Figure 2, at least substantially perpendicular to the planar surface 124 of the adhesive layer 108 and surface 128 of the substrate 132.

The product of the process is printed article 102.

The Process and Article of the Second Embodiment

Referring to Figures 3 and 4, the process and article of the second embodiment of the present invention will now be described.

In step 200, the carrier sheet 204 containing a temporary release adhesive 208 (such as wax) in the reverse of the desired pattern or image is flocked by suitable techniques, preferably electrostatically, with the flock of the present invention. The carrier locates temporarily the flock fibers and then hold flock fibers in the desired position for subsequent processing.

The carrier sheet 204 can be any suitable transfer carrier, such as dimensionally stable paper, processed paper, plastic film, resin sheets, and metal foils. Depending on the desired effect and the sheet materials employed, the carrier can be transparent, translucent, or opaque, but is typically transparent. Typically (but not always), the primary carrier is a discontinuous sheet as opposed to a continuous sheet on a running web line.

The release adhesive 208 can be any adhesive that adheres more strongly to the carrier sheet and/or to itself than the flock fibers but adheres to both enough to hold them together during storage, handling and processing. It commonly has a relatively low bonding strength with the resin film (as is commonly known for stickers or pressure-sensitive decal media). Examples of the release adhesives include a polyvinyl acetate, polyvinyl alcohol, polyvinyl chloride, polyvinyl butyral, acrylic resin, polyurethane, polyester, polyamides, cellulose derivatives, rubber derivatives, starch, casein, dextrin, gum arabic, carboxymethyl cellulose, rosin, or compositions containing two or more of these ingredients. Preferably, the release adhesive has a sufficiently low surface energy to enable even coating of the resin dispersion (applied in the next step) on the release adhesive.

In one configuration, the release adhesive is an uncured silicone adhesive. As will be appreciated, silicone adhesives are applied as a uniform coating to a surface, such as paper, and later thermally cured or radiation cured. Thermally cured systems can be classified further according to their curing mechanism as either condensation or addition (hydrosilylation) cure systems. Figure 33 shows the curing reactions of the addition cure chemistry. The primary crosslinking reaction occurs between a vinyl functional silicone polymer and a silicon-hydride functional crosslinker in the presence of a heavy metal catalyst, such as platinum or rhodium. Post-cure reactions, such as the hydrolysis of SiH groups to form silanol followed by reaction with remaining SiH groups to form a type of crosslinking, can also occur.

Silicones anchor to substrates by way of two mechanisms, namely mechanical interlocking with a substrate and chemical reactions with a substrate. Mechanical interlocking occurs when silicone adhesives are applied to semi-porous substrates, such as paper. Although mechanical interlocking preferably is substantial in the present invention, the predominant mechanism is chemical interaction with the substrate. Paper substrates include primarily cellulose fibers, sizing agents, and surface coatings or surface sizes, typically based primarily on starch, polyvinyl alcohol, sodium alginate, carboxymethylcellulose, and mixtures thereof. When silicones are coated on paper, side reactions with these components can occur. Cellulose and surface sizing agents include unreacted hydroxyl and carboxyl groups that can react with the silicone crosslinker. Figure 34 depicts several reactions that can occur between the silicone crosslinker and the paper substrate. It is these reactions that account for most of the long-term adhesion of the silicone adhesive on paper substrates.

Most addition cure systems are formulated with an excess of silicone hydride crosslinker. Typical SiH/Si-vinyl ratios are on the order of 1.2:1 to 2:1, thereby leaving unreacted SiH species after the primary crosslinking reaction (cure reaction) has occurred. These remaining unreacted species or SiOH groups from the hydrolyzed crosslinker can react with the various groups found on the paper surface. A silyl ether linkage is formed between surface OH groups and residual crosslinker. The carboxyl functionality of the substrate can form a silyl ester bond and impart silicone anchorage.

Although any silicone adhesive may be used, pressure sensitive silicone adhesives are preferred. Particularly preferred silicone adhesives include Dow Corning's 7500 Adhesive, which is screen printable, and 2013 Adhesive, which has similar properties to typical solvent-borne silicone adhesives but without the solvent. The use of these adhesives overcomes the toxicity normally associated with solvent-based adhesives.

The release adhesive 208 may be applied on the carrier in the perimeter shape of the desired design or without regard to the overall design desired. The release adhesive may be applied by any suitable technique such as, for example, by applying the release adhesive with rollers or spraying the release adhesive.

When a silicone adhesive is used as the release adhesive 208, the adhesive is applied to the, typically semi-porous or porous, carrier and flocked before the adhesive is cured. The curing is performed before the flocked surface 212 is sublimation ink printed and/or thermofixed. After curing and when PCT is the flock fiber, the force of attraction or adhesive force between the release adhesive and carrier and/or itself is greater than that between the flock fibers and the release adhesive. As a result, after removal of the carrier from the flock fibers, little, if any, release adhesive remains on the removed fibers.

The exposed ends 216 of the flocked surface 212 are then sublimation ink printed in step 220 by the techniques discussed previously. As a part of the sublimation ink printing step 112, the flock is subjected to heat and pressure to thermofix the transferred sub-ink dyes. As noted, vacuuming of the flock can be conducted preferably before or after sublimation ink printing. Commonly, the color must go all the way down the fiber, preferably to the top or first surface.

The exposed, printed ends 216 of the flocked surface are next contacted in step 226 with a binder adhesive 224, such as a water based acrylic which binds the flock together as a unit. The binder 224 adhesive may contain a hot melt adhesive for binding the printed article 228 to a desired substrate.

In optional step 230, the hot melt adhesive 232 is applied to the previously applied binder adhesive 216. After bonding of the hot melt adhesive 232 to a desired substrate, the carrier sheet 204 can be removed to permit the dye on the now exposed surface 234 to be visible.

Unlike other release adhesives, such as wax, silicone adhesives are able to withstand the thermal conditions of sublimation printing and dye particle thermofixing without melting, flowing, or otherwise loss of its bond to the carrier and flock fibers. This prevents the transfer from losing its structural integrity during or after sublimation printing. In addition to having a high thermal resistance, silicone adhesives have the further advantage of being inexpensive, having bonds of high strength, and readily available.

The Process and Article of the Third Embodiment

Referring to Figures 7-10, a third process embodiment will now be described.

In step 700, the sublimation ink is printed onto the carrier 804 by known techniques, such as lithography, letterpress, gravure, flexography, screen printing, and jet printing. As can be seen in Figure 8, the sublimation ink 808 is positioned on top of the release adhesive 812 and carrier sheet 816. Both the sublimation ink 808 and release adhesive 812 are printed on the carrier sheet 816 in the reverse of the desired pattern/design.

The preferred release adhesive is preferably a pressure-sensitive and soft film adhesive (such as an acrylic adhesive) and a hot melt adhesive (such as a compounded block rubber adhesive and a silicon rubber adhesive). Silicon release adhesives can withstand thermofixing temperatures if used properly. Acrylic and silicon release adhesives are applied to the carrier sheet 816 and cured before using them to hold the flock fibers. Pressure sensitive adhesives are generally always tacky. They can be "removable" in which case they would not leave residue on the flock fibers after the fibers are pulled off of the carrier 804.

It is possible that an uncured silicon adhesive (not a silicon pressure sensitive adhesive) can be used as a flock adhesive. The separate parts could be formulated to have sufficient viscosity to hold the flock even in the adhesive's uncured state. However, the fibers would tend to move slowly in this state because the material would be a viscous liquid.

In step 704, flock 900 is applied to the release adhesive by known techniques, such as heat and/or pressure techniques from a previously-made transfer. As can be seen from Figure 9, the flock fibers pass through the sublimation ink layer 808 and most are embedded in the release adhesive 812. In this manner, the flock fibers are maintained in a desired position and orientation during subsequent processing steps.

In step 708, the flocked article 904 is subjected to elevated temperature and pressure to cause the dye particles to thermofix the dye onto the flock fibers, preferably by vapor phase transfer of the dye particles to the flock fibers 900. In this step, the sublimation ink layer 808 effectively disappears as the carrier and component dye particles vaporize or sublime. After this step, most, if not all, of dye in the layer 808 is absent. In other words, the layer 808 is continuously distributed over the release adhesive 812 before step 708 and discontinuously distributed after step 708. During this step, the pressure applied to the flock fibers pushes the fibers down into the release adhesive, further securing the flock fibers to the carrier and maintaining the position and orientations of the flock fibers until later the fibers are pulled out of the release adhesive after heat transferring the flocked article to a desired surface. The dye can simultaneously sublime onto and into the flock fibers.

In step 712, the permanent adhesive 1000 is applied to the free ends 908 of the flock fibers 900 by suitable techniques. The permanent adhesive 1000 can be any of the adhesives noted above. The final printed article 716 is shown in Figure 10. Permanent adhesive can also firstly be applied to ends of the flock fibers.

This process embodiment colors the flock from the top (which is the end embedded in the release adhesive 812) down rather than from the bottom (which is the end embedded in the permanent adhesive 1000) up. Additionally, the sublimation ink and fibers are positioned in intimate contact with one another. Thus, the printed article 716 has superior color intensity and clarity compared to other process embodiments. It is also easier to control the deposit of the dye into the flock fibers and thereby also control the quality of the printed image.

The Process and Article of the Fourth Embodiment

Referring to Figures 5 and 6, the process and article of the fourth embodiment of the present invention will now be described.

In step 500, the carrier sheet 504 containing a temporary release adhesive 508 (such as wax) in the reverse of the desired pattern or image is flocked by suitable techniques, preferably electrostatically, with the flock of the present invention.

The exposed ends 512 of the flocked surface 516 are then sublimation printed and the dye thermofixed in step 520 by the techniques discussed previously. As noted, vacuuming of the flock can be conducted before or after sublimation ink printing.

The exposed, printed ends 512 of the flocked surface are next typically heat contacted with or laminated to a first permanent adhesive 524 in step 528. The permanent adhesive is preferably an activatable adhesive such as a thermoset or thermoplastic adhesive which may be in the form of a film or non-woven web.

In step 532, the first permanent adhesive 524 is contacted with an optional barrier film 536.

In step 544, the second permanent adhesive 540 is optionally applied to the barrier layer 536 to permanently bond the printed article 548 to a desired substrate.

As will be appreciated, step 520 can be performed after steps 528, 532, and/or 544 (any one or a multiple of which can be performed separately or simultaneously by laminating techniques) and subsequent removal of the carrier sheet to provide a surface for printing.

As will be further appreciated, during thermal activation of the hot melt adhesive setting/thermofixing of the dye applied by sublimation ink printing step 520 (using inkjet techniques) can be performed when sublimation ink printing is done after steps 528, 532, and 544. This eliminates a separate process step to set the adhesive.

The Process and Article of the Fifth Embodiment

Figures 14A-14B depict a process and article of a fifth embodiment of the present invention. This process is particularly useful where higher energy dyes in sublimation printing inks are employed, requiring higher temperatures during sublimation printing.

The flocked thermosetting adhesive film 2300 is formed by applying flock 2400, such as by direct flocking or lamination techniques, to a pre-formed solidified thermosetting film 2404. The thermosetting adhesive film may be partially or fully activated before or during the sublimation printing step 2304 and is not activated or only partially activated before the flock is applied to the film 2300.

In the sublimation printing and thermofixing step 2304, the flocked film 2300 is sublimation printed and the dye thermofixed by any of the techniques referenced herein to

provide a printed design 2308. The printed design 2308 includes the desired design transferred to the flock and/or adhesive film 2404.

In step 2312, a second adhesive film, such as a thermosetting or thermoplastic adhesive, is applied to the thermosetting adhesive 2404, preferably by laminating techniques using a pre-formed, solidified thermosetting or thermoplastic adhesive film. The temperature at which the second adhesive film is applied to the printed design 2308 is lower than the maximum temperature experienced by the flock during sublimation printing. The temperature range used during sublimation printing has been noted previously. The temperature range for laminating the second adhesive film 2408 to the (fully activated) thermosetting adhesive typically is no more than about 375 degrees Fahrenheit, more typically no more than about 350 degrees Fahrenheit. In a preferred configuration, the second adhesive is a thermoplastic polyester adhesive film, such as a polycarbonate adhesive. The printed article 2316 has the configuration of Fig. 14B.

The Process and Article of the Sixth Embodiment

Figures 16-21 depict a process and article of a sixth embodiment of the present invention. This process is particularly useful where a fully sublimation printed flock fiber is desired. The processes of many of the foregoing embodiments print colors onto the fibers from the free ends, sides, or bottoms (attached ends) of the fibers. Such printing techniques dyes can have limits as to how long a fiber can be printed due to the difficulty of moving the dye a selected distance, while controlling color intensity, shade and hue. The process of the sixth embodiment attempts, at least partially, to address this issue. The further that it must be transported and penetrate a flock fiber, the more energy is needed and consequently the process is more difficult to control.

With reference to Figures 16 and 17, a first flocked carrier sheet 2600 is provided. The first flocked carrier sheet 2600 includes a first sacrificial carrier sheet 2700, a first release adhesive 2704 adhered to the first carrier sheet 2700, and flock 2708 adhered to the first release adhesive 2704. The first sacrificial carrier sheet 2700 and release adhesive 2704 can be any of the materials discussed above.

In step 2604, a design is (direct or transfer) sublimation printed on the first flocked carrier sheet 2600 using any of the techniques noted previously to provide a first printed design 2608. For example, the sublimation printing can be performed from the attached or free ends 2712 or sides of the flock 2708.

In step 2612 which may be performed at the same time as step 2604, the various dye(s) in the printed design are thermofixed by the techniques noted above.

In step 2616, the first (free) ends 2712 of the flock are contacted with a second sacrificial carrier sheet 2804 and second release adhesive 2800 by suitable techniques to form a second printed flocked carrier sheet assembly 2808 (shown in Figure 28). For example, the first flocked carrier sheet 2600 can be in the form of a web or roll that is pressure contacted with a web or roll of the second carrier sheet/release adhesive using as a roller assembly. The adhesive or bonding strength of the first release adhesive 2704 is less than that of the second release adhesive 2800. For example, the first release adhesive 2704 can be wax or silicone while the second release adhesive 2800 is a thermoplastic, heat-activated, or pressure sensitive adhesive. The second (attached) ends 2808 of the flock is still attached to the first carrier sheet 2700 and release adhesive 2704.

In step 2620, the first carrier sheet 2700 and release adhesive 2704 are removed from the second printed flocked carrier sheet assembly 2808 to provide a second printed flocked carrier sheet 2624. With reference to Figure 19, the second printed flocked carrier sheet 2624 includes the flock 2708 and second release adhesive 2800 and carrier sheet 2804.

In step 2628, a first permanent adhesive 3000 is applied to the second (free) ends 2808 of the flock 2712. The first ends 2712 of the flock 2708 are attached to the second release adhesive 2800. The first permanent adhesive may be in the form of a pre-formed solid film or liquid adhesive before step 2628. When the adhesive 3000 is a thermosetting adhesive, the solid film adhesive may be partially set or activated during the application step 2628. When the adhesive 3000 is a thermoplastic adhesive, the adhesive is heated to a sufficient temperature to adhere the adhesive to the flock 2708. As will be appreciated, the bonding strength of the first permanent adhesive 3000 exceeds that of the second release adhesive 2800.

When the adhesive 3000 is applied as a liquid, optional step 2632 may be performed to add a second permanent adhesive 3100 to the exposed end of the first permanent adhesive 3000. For example, the first permanent adhesive 3000 may be a printed latex, such as a thermosetting liquid acrylic adhesive, and the second permanent adhesive 3100 a thermoplastic powdered adhesive. This process embodiment can provide finer freestanding adhesive lines for the design than with, for example, solid films from which the final design shape must be cut out. As will be appreciated, the first and second permanent adhesives may both be thermosetting or thermoplastic adhesives.

Alternatively, the first permanent adhesive 3000 may be a thermoplastic while the second permanent adhesive 3100 is a thermosetting adhesive.

Figure 21 depicts the printed article 2636 assuming that step 2632 is performed. When step 2632 is not performed, the printed article 2636 has the configuration of Figure 31 except that the second permanent adhesive layer 3100 is omitted.

The process of Figure 16 is a double-transfer-type process, which, though costly when performed discontinuously, can be automated on a one-pass continuous line to provide a cost effective process alternative.

The Process and Article of the Seventh Embodiment

Figures 11-13 depict a process and article of a seventh embodiment of the present invention. In this embodiment, the flock fiber is heat set during or after thermofixing.

In step 1100, sublimation ink is printed onto the carrier 1200 in the reverse of the desired pattern. The ink is printed on the carrier sheet 1204 between the carrier sheet 1204 and release adhesive 1208 or on top of the release adhesive 1208. The flock 1212 may be applied to and embedded in the release adhesive 1208 before, during, or after sublimation printing of the ink onto the carrier 1200.

In steps 1104 and 1108, the carrier 1200 and flock 1212 are contacted with ghosting paper 1216 and the assembly subjected to heat and pressure to thermofix the dye particles into the flock fibers and heat set the flock fibers. Ghosting paper 1216 is commonly not adhered to the free ends 1220 of the flock fibers 1212. The ghosting paper covers the tips of the fibers to absorb and prevent the dye particles from dispersing away from the fibers. If the dye particles disperse away from the fibers, dye particle penetration into the fibers and color intensity is decreased. The ghosting paper absorbs excess dye particles. The ghosting paper further holds the fibers 1212 in a desired position and orientation during the thermofixing and heat setting steps 1104 and 1108. Ghosting paper is soft and readily deforms and conforms to the contours of the ends 1220 of the fibers.

For optimized transfer of the dye to the fibers, the absorbencies of the ghosting paper and carrier should be lower than that of the fibers and the ghosting paper and the carrier sheet should not soften at transfer temperatures. Absorbency is commonly measured by the oil absorption value.

When step 1104 is performed before step 1108, the fibers are further heated in step 1108 to an elevated temperature relative to the thermofixing temperature in step 1104. Typically, the flock fiber temperature in step 1108 is at least about 220°C and more

typically at least about 20°C greater than the maximum temperature during thermofixing. The flock fiber temperature in step 1108 commonly ranges from about 210 to about 240°C (for PCT).

Performing step 1104 before the fiber is heat set can have benefits. Dye particle penetration is greater in the amorphous phase of a material rather than the crystalline phase of the material. Heat setting increases the proportion of the flock fiber polymeric constituents that is crystalline compared to the amorphous phase. Thus, heat setting after thermofixing provides greater dye particle penetration into the flock fiber as the flock fiber polymeric constituent has a greater proportion of amorphous phase material than crystalline phase material compared to the flock fiber polymeric constituent after heat setting 1108. Moreover, heat setting and increasing the crystalline phase proportion of the fiber polymeric constituent helps to molecularly "lock" the dye particles in the fiber matrix, providing a higher degree of color fastness.

Because material that has not been heat set will experience greater shrinkage during thermofixing than heat set material, the fiber may be cut to a longer length to account for the shrinkage without compromising the plushness and hand of the article. Preferably, the fiber length ranges from about 1 to about 1.5 mm in length.

EXPERIMENTAL

The flock fiber deformation temperature was evaluated for a number of polymers, namely nylon 6,6, PET, PCT, and PCTA™ (shown as being PCX). The experiment was performed using a microscope with a hot stage and measuring system. The results are presented in Figs. 22 and 32 and Table I below.

Material	**Polymer Tg**	**Flock T deform**	**Flock Tm**	**Polymer Tm**
Polyesters				
PET	70-77	145	251	256-284
PTT PCT	92		270*	290-318
PCTA™	100			180-200
Polyamides				
Nylon 6	50-75			214-233
Nylon 6.6	45-57		256	250-272
MXD6™	90			245

* No melting on first heat where Tg is the glass transition temperature, Tdeform is the deformation temperature and Tm is the melting temperature.

As can be seen from the above, PET began to deform at a temperature of approximately 130°C while PCT and PCTA™ began to deform at a temperature of approximately 200°C. Although both PET and PCTA™ have a melting point much higher than 200°C (which is the thermal region in which sublimation direct and transfer printing is performed), PCT and PCTA™ did not deform until a much higher temperature compared to PET. For free-standing flock fibers, such as electrostatically deposited flock, the thermal stability of PCT and PCTA™ can be important for sublimation ink printing. This graph further shows that, if one of ordinary skill in the art considered the thermal characteristics of PET in determining whether terephthalate polymers could be successfully sublimation printed as free-standing flock fibers, he would likely not consider this family of polymers to be viable.

Sheets comprising PCT flock fibers were dye printed with high energy dyes using direct dye printing techniques and printing and thermal treatment or curing temperatures and times normally used for nonpolyester flock fibers. The flock fibers successfully accepted the dye. The light fastness of the dyed flock was then tested in a fadometer to determine if the dyed flock met automotive specifications. The dye was found to have the required degree of light fastness to meet certain automotive specifications.

Other sheets comprising PCT flock fibers were heat transfer printed with high energy dyes. The dyed flock fibers were then subjected to crock testing, which is a standard test for dyed textiles. The dyed PCT flock fibers passed the tests.

A number of variations and modifications of the invention can be used. It would be possible to provide for some features of the invention without providing others.

For example in one alternative embodiment, other polymers, copolymers and polymer blends having one or more of the properties discussed above may be used as the flock fiber in the present invention. Examples of other suitable polymers include poly(phenylene sulfide) or PPS, a liquid crystal polymer or LCP, a high temperature polyamide, copolymers include poly(ethylene terephthalate co-1,4-cyclohexylene dimethylene terephthalate), co-polyesters including PCTA, polyesters including poly(1,3 propylene terephthalate) which is also called poly trimethylene terephthalate (PTT) or Corterra, and blends include blends of PET and PCT. A family of polymers including PTT is shown in Fig. 23, which depicts a monomer with “R” representing independently hydrogen or a substituted or unsubstituted alkyl or aryl group.

In another alternative embodiment, sublimation ink printing is not performed but the dye is spun into the polymer, copolymer, or polymer blend by known techniques. In this event, flocking could be done by any of the multi-color flocking techniques referred to above.

In another embodiment, the polymer can include glass fibers, other blend compatible polymers and/or can be copolymerized with isophthalic acid, sebacic acid and various diols. Examples of such polymer blends include the Thermx PCT polyesters CG007, CG033, CGT33, CG 053, CG907, CG923, CG933, and CG943 by Eastman Chemical Company.

In yet another embodiment, sublimation dyes are on the carrier sheet itself. In this embodiment, the sublimation transfer design is printed onto the carrier (which is preferably paper and not a plastic film) and the release adhesive is thereafter applied to the carrier over the printed dyes or vice versa. Simultaneously upon heat transferring the flocked transfer, the sublimation dye particles vaporize and recondense on the flock. The release adhesive is selected to vaporize or melt at the sublimation temperature to permit the dyes to be transferred from the sheet to the flock. This process is similar to the product sold under the name SUBLI-FLOCK™. The process is particularly useful with the second and third embodiments in which case the sublimation ink printing step would occur simultaneously with bonding of the hot melt adhesive 232 or first or second adhesive as appropriate, to a desired substrate.

In yet another embodiment, an UltraViolet or UV inhibitor can be employed to provide improved resistance to fading from ultraviolet radiation. The UV inhibitor(s) can be in the sublimation ink/dye formulation and/or be pre-applied to or incorporated into the textile substrate itself. For example, the inhibitor(s) can be included in the release adhesive layer, carrier sheet, or any of the permanent adhesive layer(s). In addition or alternatively, the UV inhibitor may be incorporated into the flock fibers themselves such as when the fibers are spun.

In yet a further embodiment, predrying of the fiber before heat setting may permit heat setting to occur at a lower temperature. Moreover, predrying of the fiber may obviate the need to heat set the polymer before thermofixing.

The present invention, in various embodiments, includes components, methods, processes, systems and/or apparatus substantially as depicted and described herein, including various embodiments, subcombinations, and subsets thereof. Those of skill in the art will understand how to make and use the present invention after understanding the

present disclosure. The present invention, in various embodiments, includes providing devices and processes in the absence of items not depicted and/or described herein or in various embodiments hereof, including in the absence of such items as may have been used in previous devices or processes, e.g., for improving performance, achieving ease and\or reducing cost of implementation.

The foregoing discussion of the invention has been presented for purposes of illustration and description. The foregoing is not intended to limit the invention to the form or forms disclosed herein. In the foregoing Detailed Description for example, various features of the invention are grouped together in one or more embodiments for the purpose of streamlining the disclosure. This method of disclosure is not to be interpreted as reflecting an intention that the claimed invention requires more features than are expressly recited in each claim. Rather, as the following claims reflect, inventive aspects lie in less than all features of a single foregoing disclosed embodiment. Thus, the following claims are hereby incorporated into this Detailed Description, with each claim standing on its own as a separate preferred embodiment of the invention.

Moreover, though the description of the invention has included description of one or more embodiments and certain variations and modifications, other variations and modifications are within the scope of the invention, e.g. as may be within the skill and knowledge of those in the art, after understanding the present disclosure. It is intended to obtain rights which include alternative embodiments to the extent permitted, including alternate, interchangeable and/or equivalent structures, functions, ranges or steps to those claimed, whether or not such alternate, interchangeable and/or equivalent structures, functions, ranges or steps are disclosed herein, and without intending to publicly dedicate any patentable subject matter.

What is claimed is:

1. An article, comprising:

a substrate;

a permanent adhesive; and

a plurality of fibers adhered by the permanent adhesive to the substrate, wherein the fibers comprise poly(cyclohexylene-dimethylene terephthalate), wherein the fibers are free-standing and oriented transversely to the adjacent surface of the substrate and wherein the fibers comprise at least one of a medium and high energy sublimation dye.

2. The article of claim 1, wherein the at least one of a medium and high energy dye is a medium energy dye.

3. The article of claim 2, wherein the fibers are heat set, extruded, and/or drawn at a temperature of at least about 215°C and wherein the fibers are flock.

4. The article of claim 1, wherein the at least one of a medium and high energy dye is a high energy dye.

5. The article of claim 4, wherein the fibers are heat set, extruded, and/or drawn at a temperature of at least about 220°C and wherein the fibers are flock.

6. A method, comprising:

providing a carrier, the carrier comprising a carrier substrate, a release adhesive, and a sublimation ink layer, wherein the sublimation ink layer is at least one of (i) located between a first surface of the carrier substrate and a second surface of the release adhesive and (ii) located on a first surface of the release adhesive, the first and second surfaces of the release adhesive being in an opposing relationship;

applying fibers to the carrier, wherein the fibers contact the first surface of the release adhesive and have first and second ends, the second ends being adhered to the first surface of the release adhesive;

thermofixing the dye particles in the sublimation ink to the fibers to color the fibers; and

applying a permanent adhesive to the first ends of the fibers.

7. The method of claim 6, wherein the release adhesive is at least one of a pressure sensitive adhesive and hot melt adhesive and wherein the permanent adhesive is at least one of a thermoplastic and thermoset adhesive, and wherein the permanent adhesive absorbs at least some of the dye particles such that the permanent adhesive has a color substantially the same as the color of fibers embedded in the permanent adhesive.

8. The method of claim 6, wherein the fibers are flock fibers and wherein the flock fibers comprise a polyester.

9. The method of claim 6, wherein the at least one of (i) located between a first surface of the carrier substrate and a second surface of the release adhesive and (ii) located on a first surface of the release adhesive is (i).

10. The method of claim 6, wherein the at least one of (i) located between a first surface of the carrier substrate and a second surface of the release adhesive and (ii) located on a first surface of the release adhesive is (ii).

11. The method of claim 6, wherein the sublimation ink layer is substantially absent after the thermofixing step.

12. The method of claim 6, wherein the sublimation dye ink comprises at least one of a medium energy and high energy dye.

13. The method of claim 6, wherein the fibers comprise at least about 25 wt.% of a terephthalate polymer and/or copolymer having a repeating unit of the formula of Figure 15 or 23, where "R" represents independently hydrogen or a substituted or unsubstituted alkyl or aryl group and "S" is an aromatic or nonaromatic cyclic residue which can include one or more hereoatoms.

14. The method of claim 6, wherein the polymer has a glass transition temperature of at least about 75°C, and wherein the fibers have an aspect ratio similar to that of nylon and a denier of from about 2 to about 50.

15. The method of Claim 12, wherein the polymer is poly(cyclohexylene-dimethylene terephthalate and the fibers are flock.

16. A method, comprising:

providing a fiber-containing surface, the fibers comprising a polyester;

thermofixing dye particles in a sublimation ink onto the fibers, wherein the fibers are free of heat setting before the thermofixing step;

heat setting the fibers; and

applying a permanent adhesive to free ends of the fibers to form a printed article.

17. The method of claim 16, wherein the polyester has a deformation temperature at or above a maximum fiber temperature during the thermofixing step and wherein the sublimation ink is located on a release adhesive included in the fiber-containing surface.

18. The method of claim 16, wherein the fibers are flock fibers and wherein the lengths of the flock fibers ranges from about 1 to about 1.5 mm.

19. The method of claim 16, wherein the polyester has a glass transition temperature of at least about 75 degrees Celsius and is heat set at a temperature at or above a maximum fiber temperature in the thermofixing step.

20. The method of claim 16, wherein the thermofixing step is performed with a high energy dye.

21. The method of claim 16, wherein the thermofixing step is performed with a medium energy dye.

22. The method of claim 16, wherein the heat setting and thermofixing steps occur simultaneously.

23. The method of claim 16, wherein the heat setting step occurs after the thermofixing step.

24. The method of claim 16, wherein the polyester comprises poly(1,3 propylene terephthalate).

25. The method of claim 16, wherein the polyester before the heat setting step has a higher degree of amorphous phase than the polyester after the heat setting step.

26. A process for sublimation printing a design into a plurality of flock fibers, comprising:

(a) providing a first flocked carrier sheet comprising a fibers, a first carrier sheet, and a first release adhesive adhering second ends of the fibers to the first carrier sheet;

(b) sublimation printing a design onto the fibers to form a first printed flocked carrier sheet;

(c) contacting first ends of the fibers in the first printed flocked carrier sheet with a second release adhesive adhered to a second carrier sheet to form a second printed flocked carrier assembly, wherein the bonding strength of the second release adhesive is greater than that of the first release adhesive and the second release adhesive is positioned between the flock and the second carrier sheet;

(d) removing the first carrier sheet from the second ends of the fibers in the second printed flocked carrier assembly to form a second printed flocked carrier sheet; and

(e) applying a permanent adhesive to the exposed, second ends of the fibers to provide a printed article.

27. The method of claim 26, wherein the sublimation printing step thermofixes a high energy dye on the fibers.

28. The method of claim 26, wherein the sublimation printing step thermofixes a medium energy dye on the fibers.

29. A method, comprising:

providing a first flocked article; the first flocked article comprising flock fibers adhered to a thermosetting adhesive, wherein the thermosetting adhesive is not yet thermoset; and

thermofixing dye particles on the flock fibers, wherein the thermosetting adhesive is thermoset during the thermofixing step.

30. The method of claim 29, further comprising:

applying a second permanent adhesive to the thermoset adhesive.

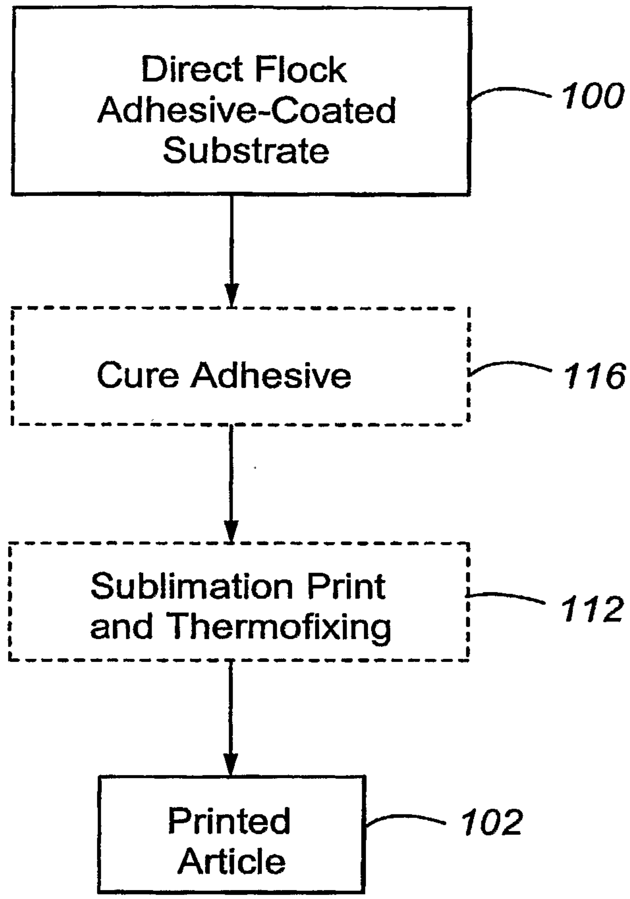
Direct Flock Adhesive-Coated Substrate
100
Cure Adhesive
116
Sublimation Print and Thermofixing
112
Printed Article
102

Fig. 1

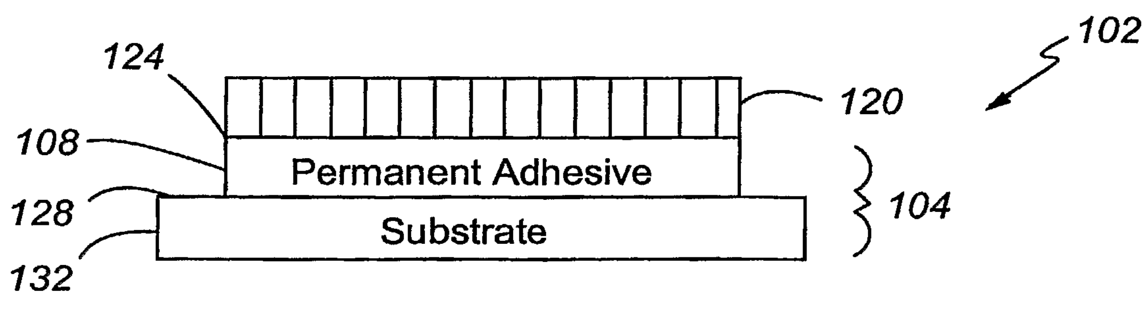
102
124
120
108
Permanent Adhesive
128
Substrate
104
132

Fig. 2

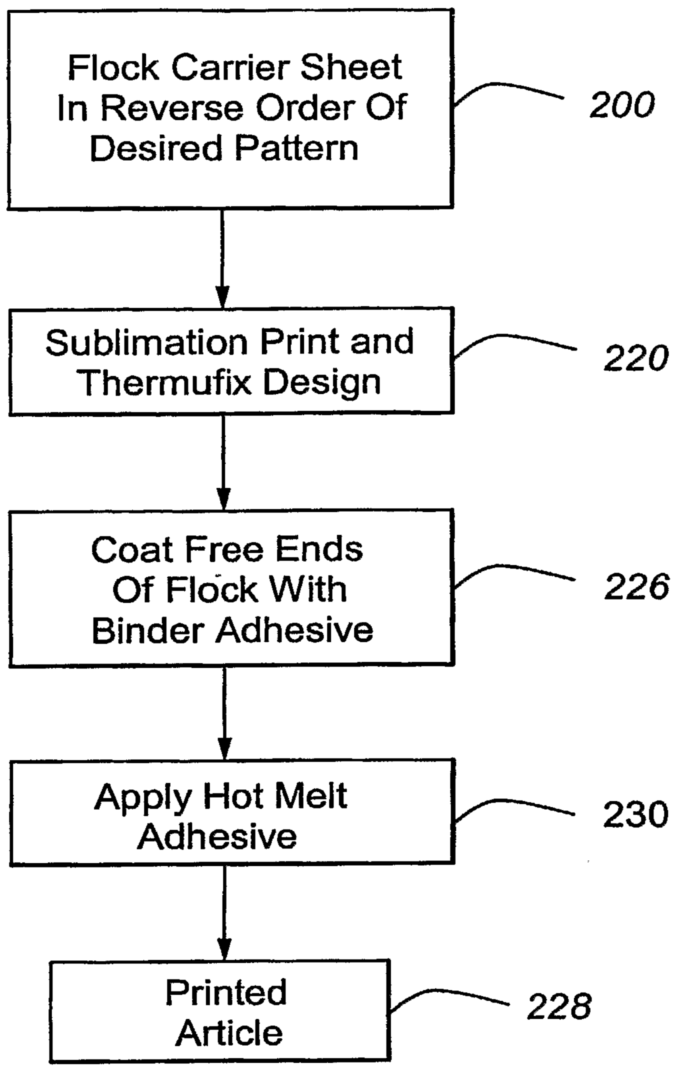
Flock Carrier Sheet In Reverse Order Of Desired Pattern
200
Sublimation Print and Thermufix Design
220
Coat Free Ends Of Flock With Binder Adhesive
226
Apply Hot Melt Adhesive
230
Printed Article
228

Fig. 3

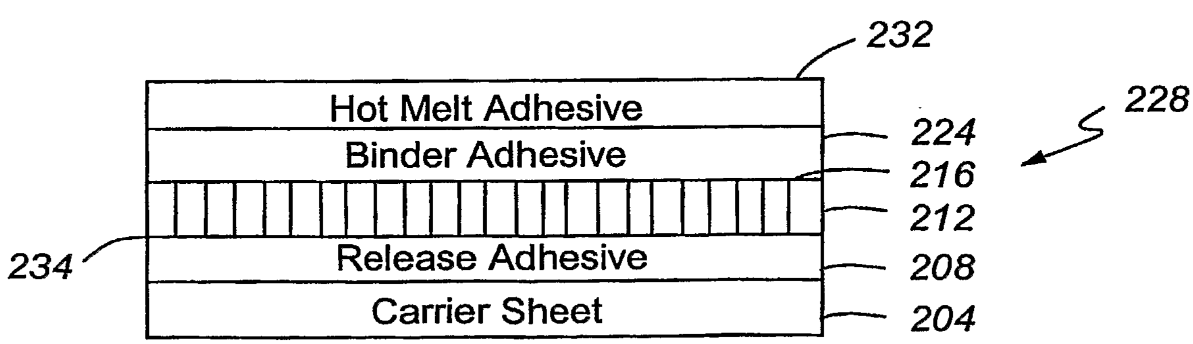
232
228
Hot Melt Adhesive
224
Binder Adhesive
216
212
234
Release Adhesive
208
Carrier Sheet
204

Fig. 4

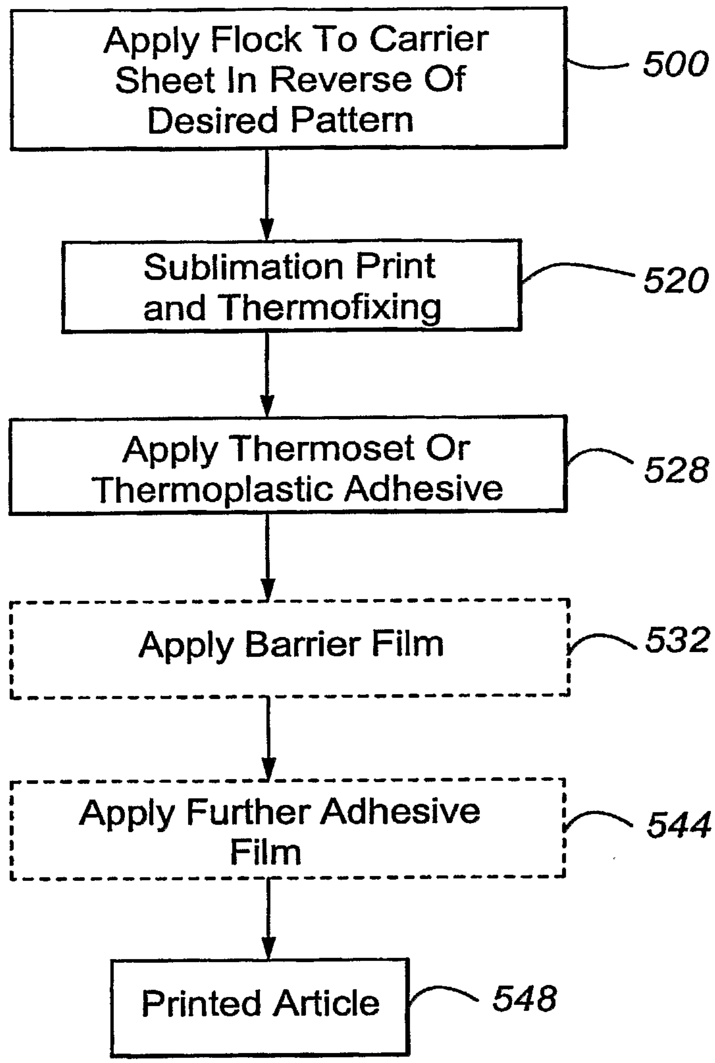
Apply Flock To Carrier Sheet In Reverse Of Desired Pattern
500
Sublimation Print and Thermofixing
520
Apply Thermoset Or Thermoplastic Adhesive
528
Apply Barrier Film
532
Apply Further Adhesive Film
544
Printed Article
548

Fig. 5

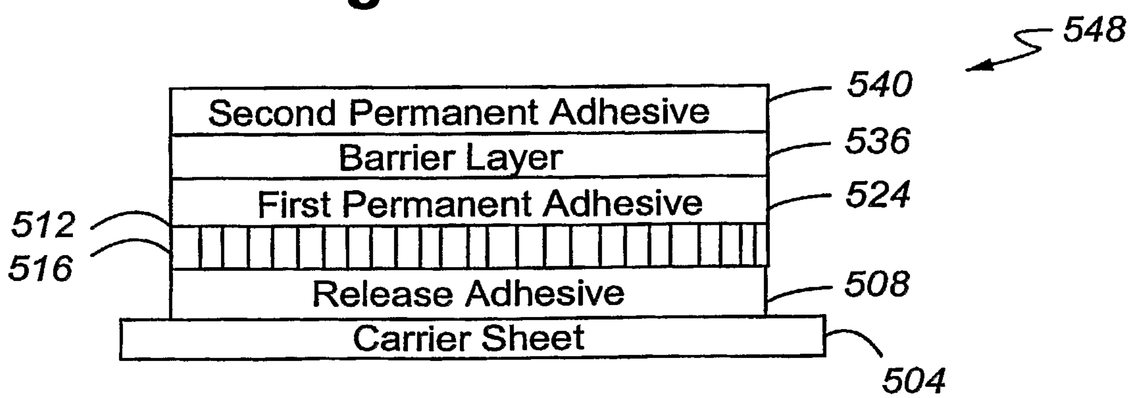
548
Second Permanent Adhesive
540
Barrier Layer
536
First Permanent Adhesive
524
512
516
Release Adhesive
508
Carrier Sheet
504

Fig. 6

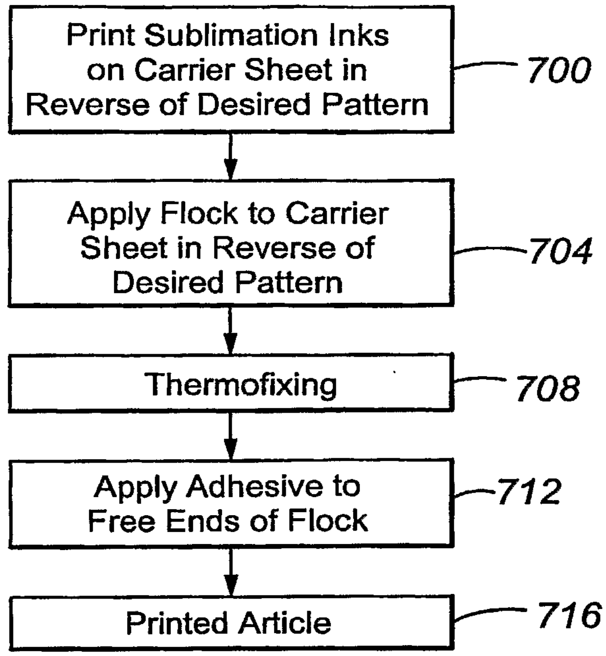

Fig. 7

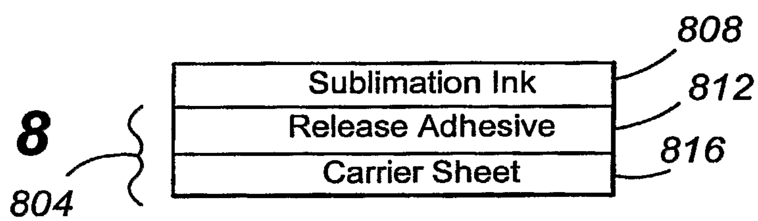

Fig. 8

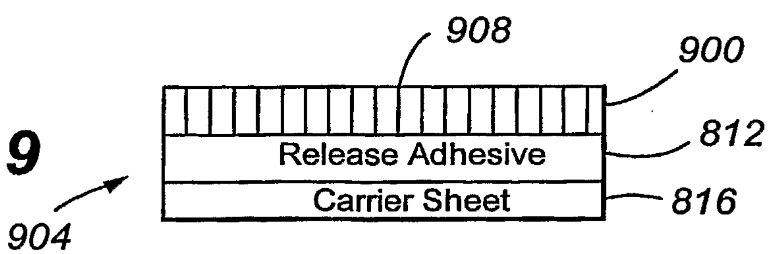

Fig. 9

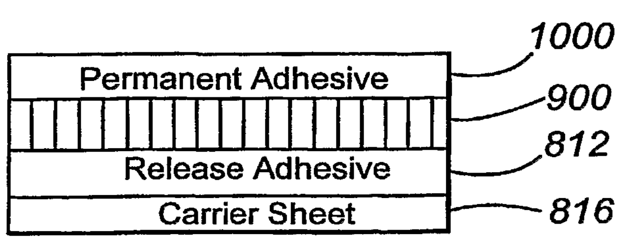

Fig. 10

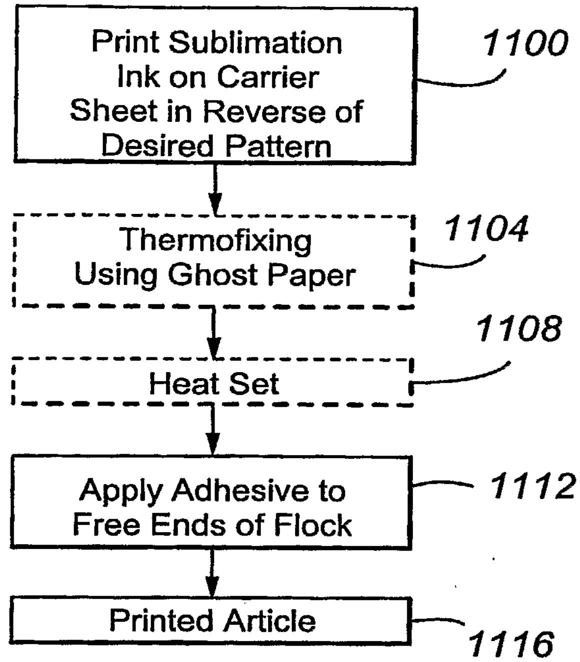

Fig. 11

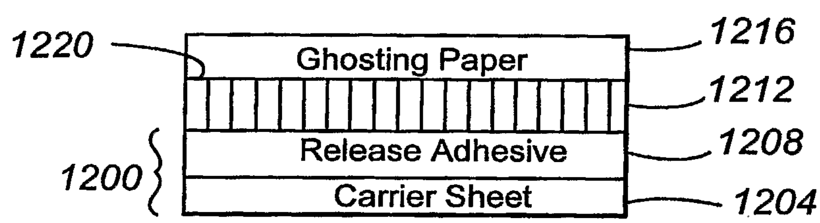

Fig. 12

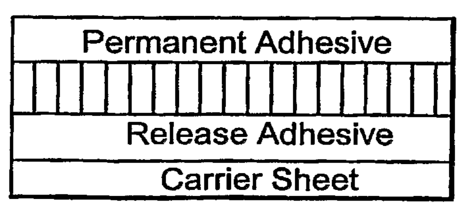

Fig. 13

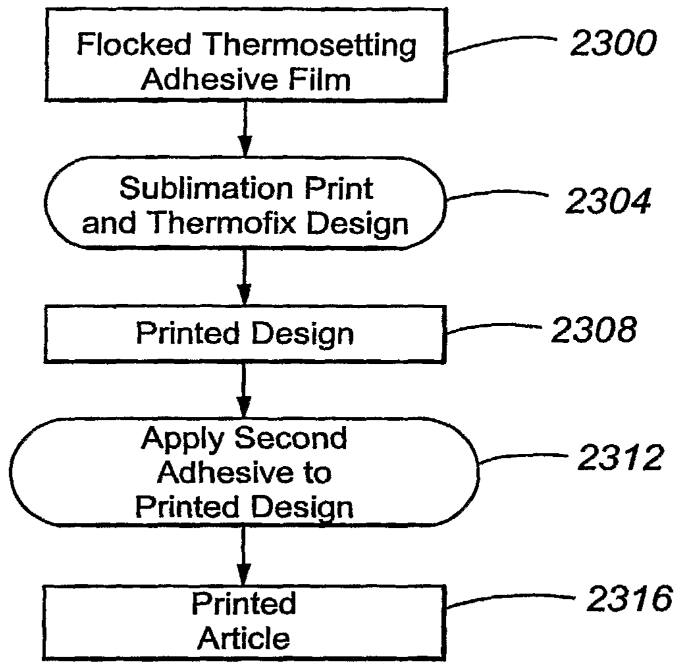

Fig. 14A

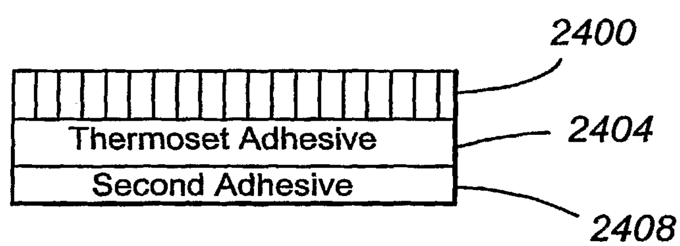

Fig. 14B

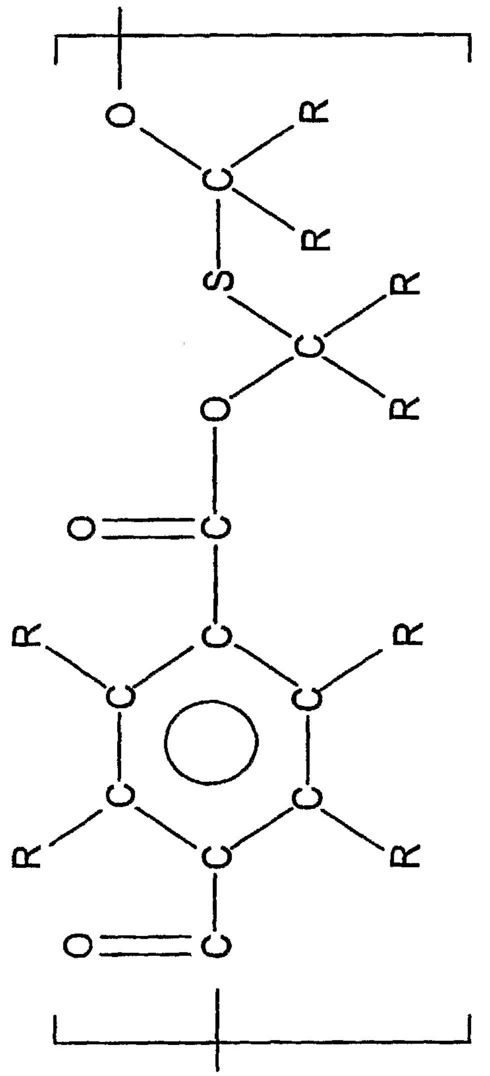

Fig. 15

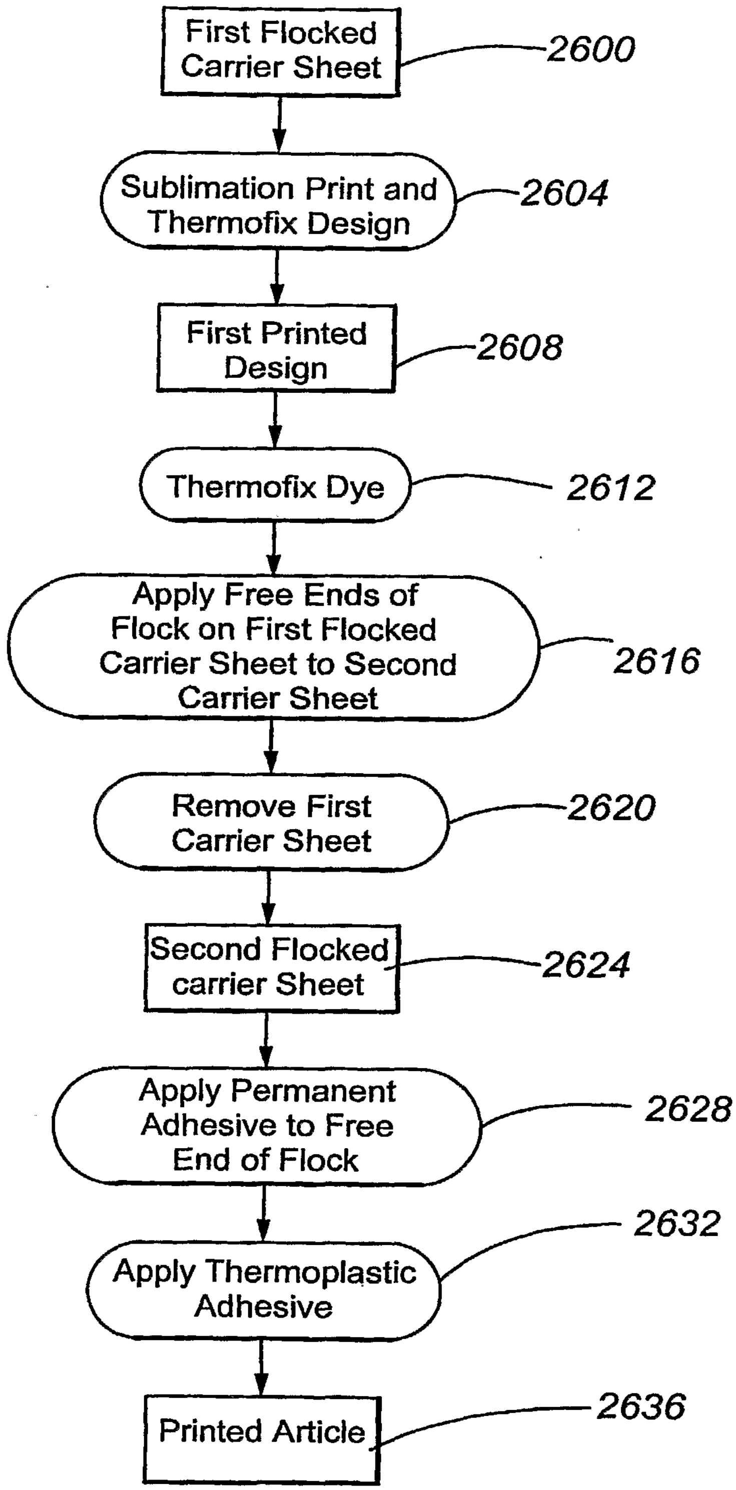
First Flocked Carrier Sheet
2600
Sublimation Print and Thermofix Design
2604
First Printed Design
2608
Thermofix Dye
2612
Apply Free Ends of Flock on First Flocked Carrier Sheet to Second Carrier Sheet
2616
Remove First Carrier Sheet
2620
Second Flocked carrier Sheet
2624
Apply Permanent Adhesive to Free End of Flock
2628
Apply Thermoplastic Adhesive
2632
Printed Article
2636

Fig. 16

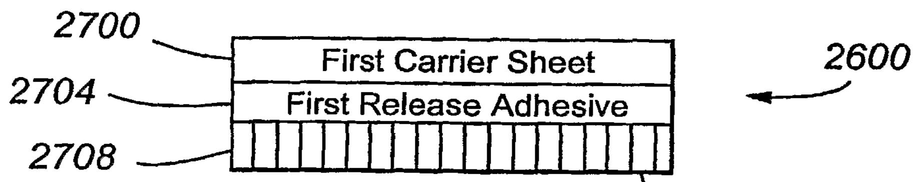

Fig. 17

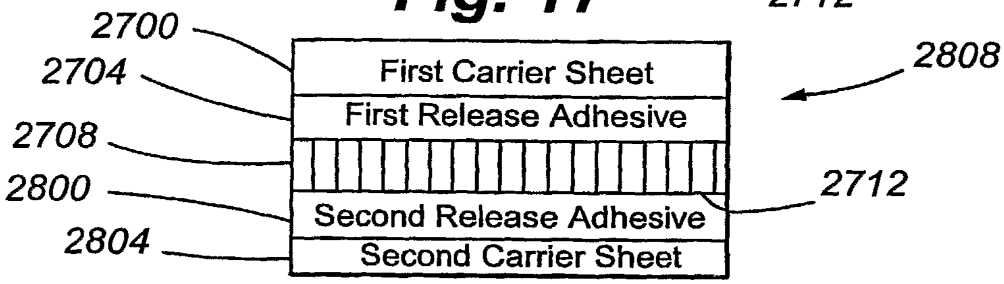

Fig. 18

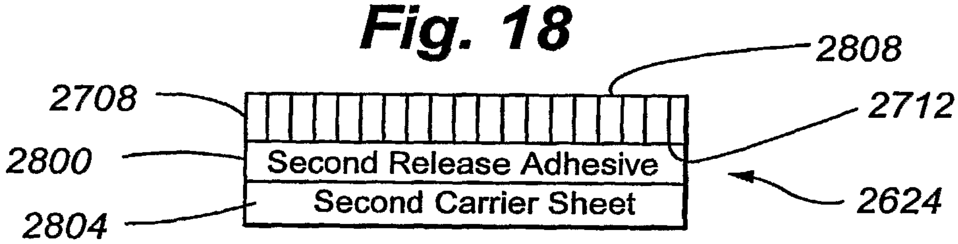

Fig. 19

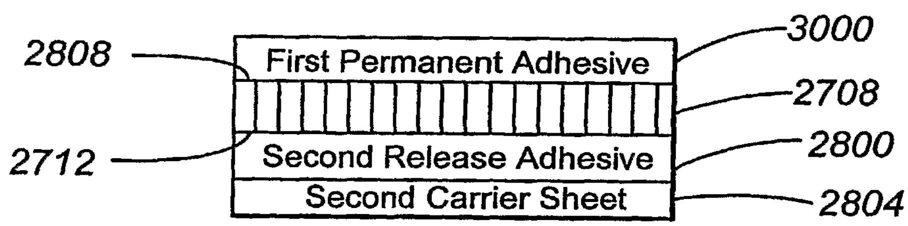

Fig. 20

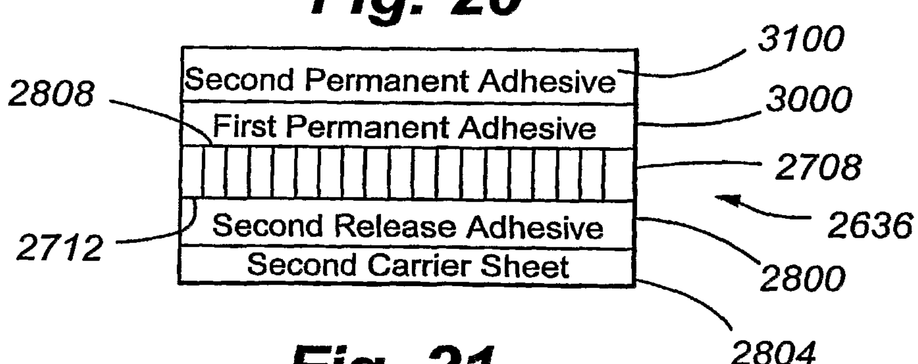

Fig. 21

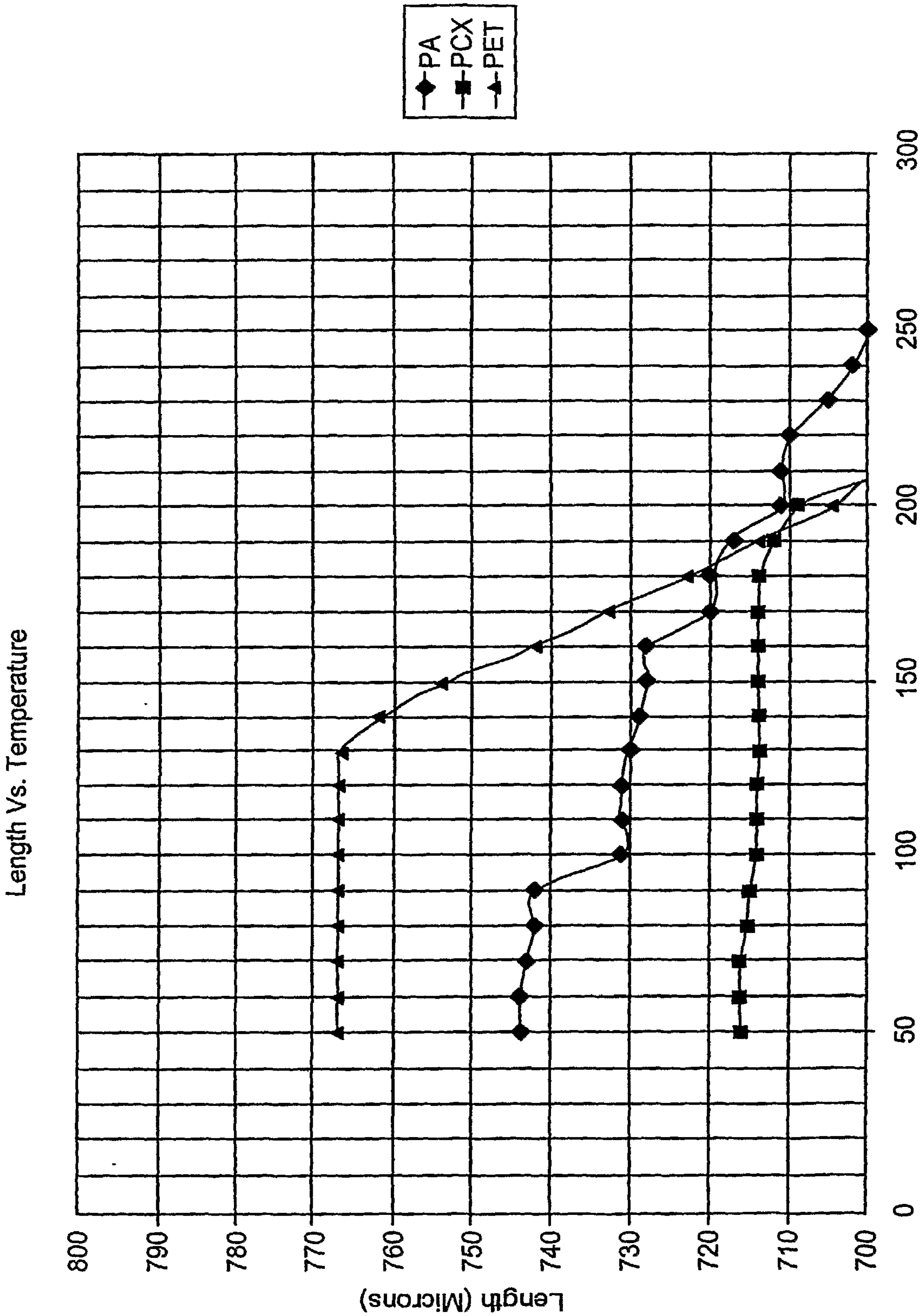
Length Vs. Temperature
Length (Microns)
Temperature (C)
PA
PCX
PET
800
790
780
770
760
750
740
730
720
710
700
0
50
100
150
200
250
300

Fig. 22

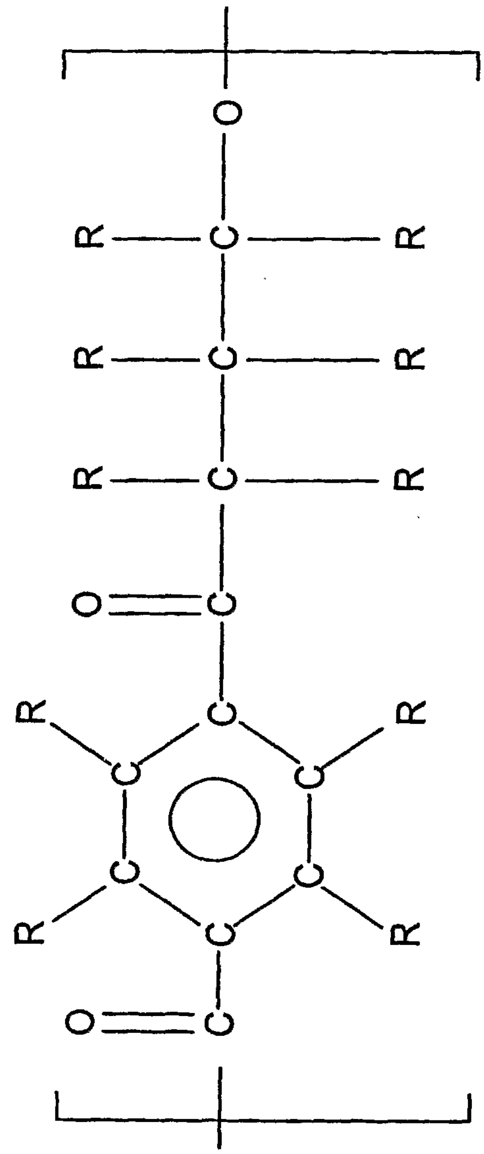

Fig. 23

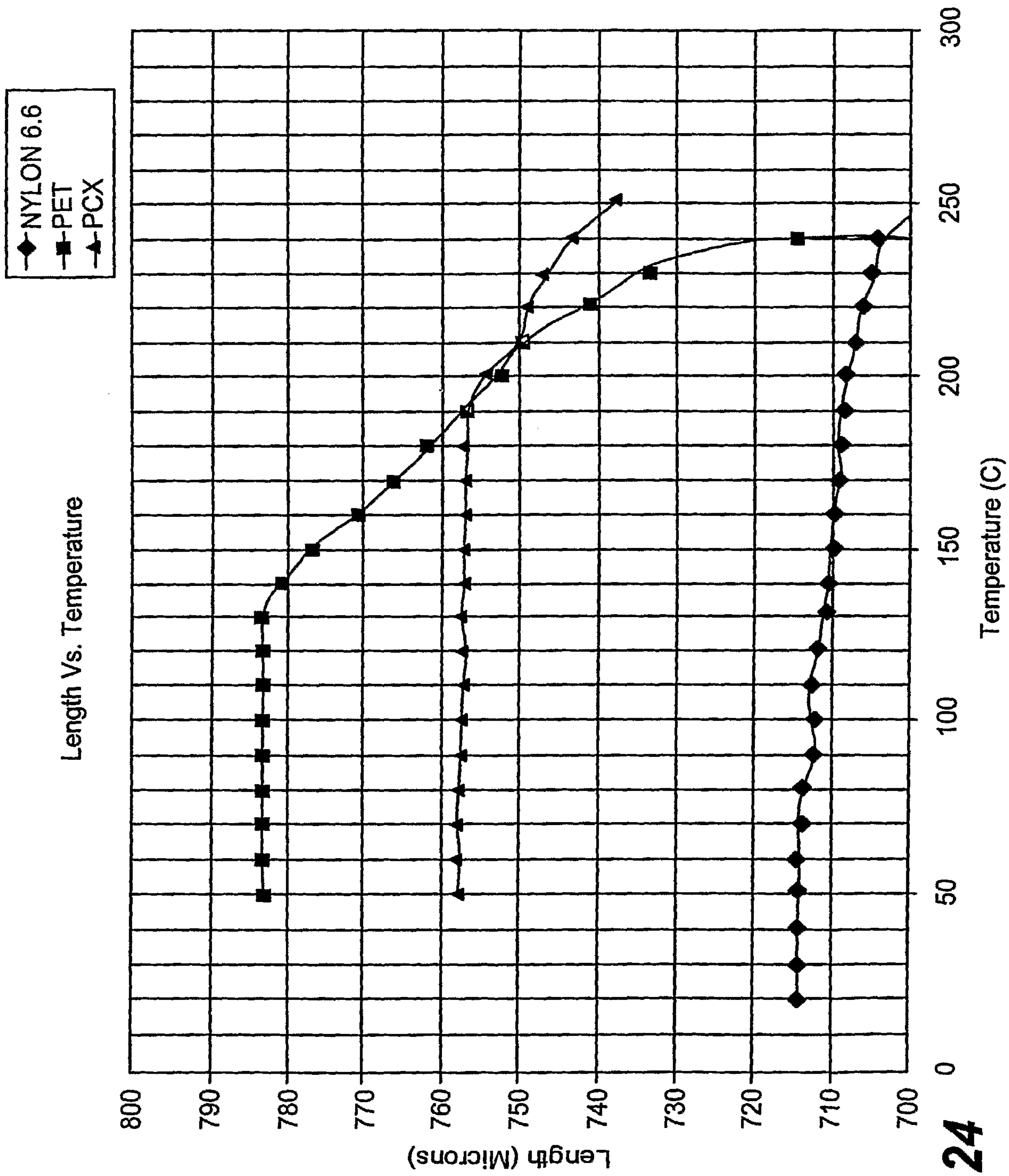
Length Vs. Temperature
NYLON 6.6
PET
PCX
Length (Microns)
800
790
780
770
760
750
740
730
720
710
700
0
50
100
150
200
250
300
Temperature (C)

Fig. 24

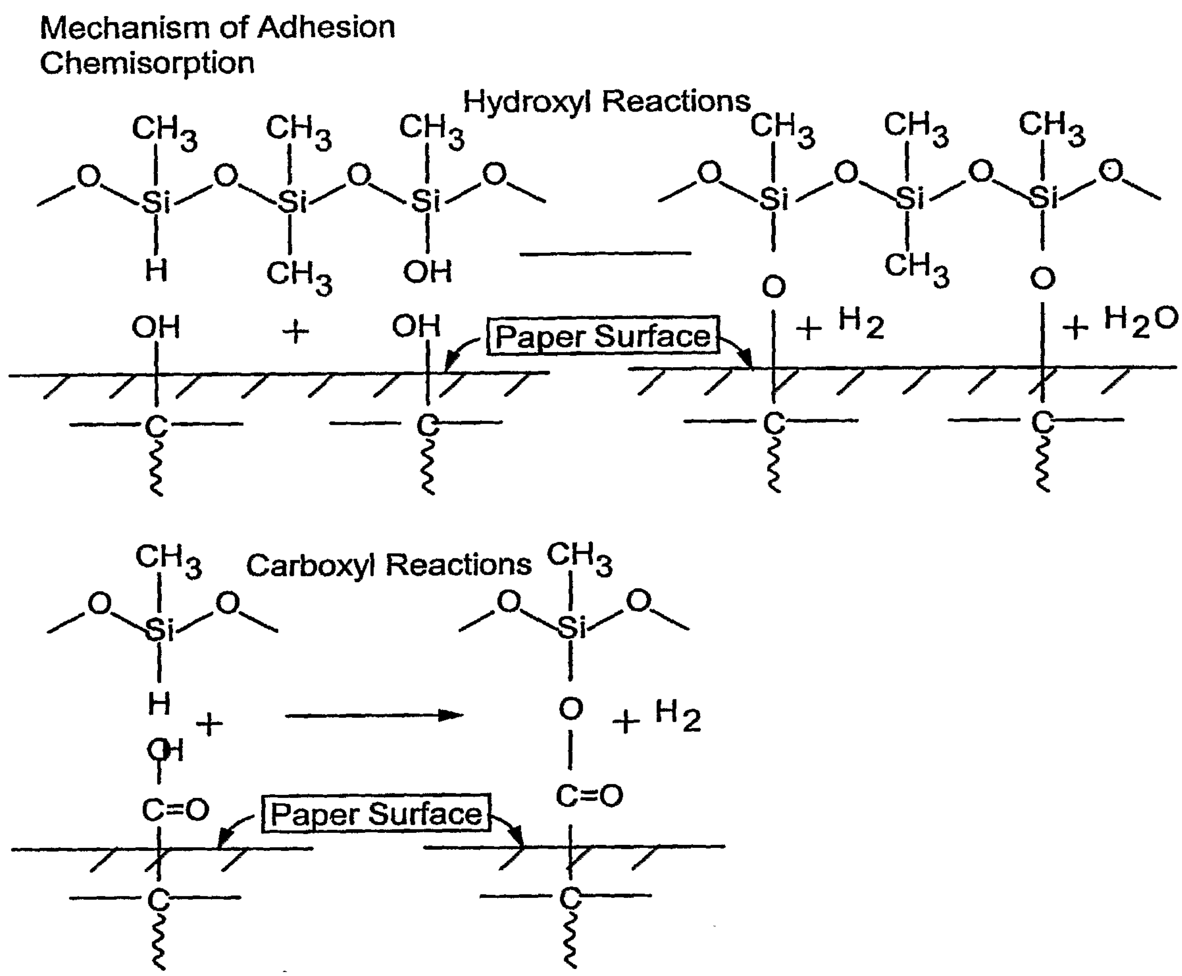
Mechanism of Adhesion
Chemisorption
Hydroxyl Reactions
CH3
O
Si
H
OH
CH3
OH
+
Paper Surface
+ H2
+ H2O
C
Carboxyl Reactions
C=O
+ H2

Fig. 26

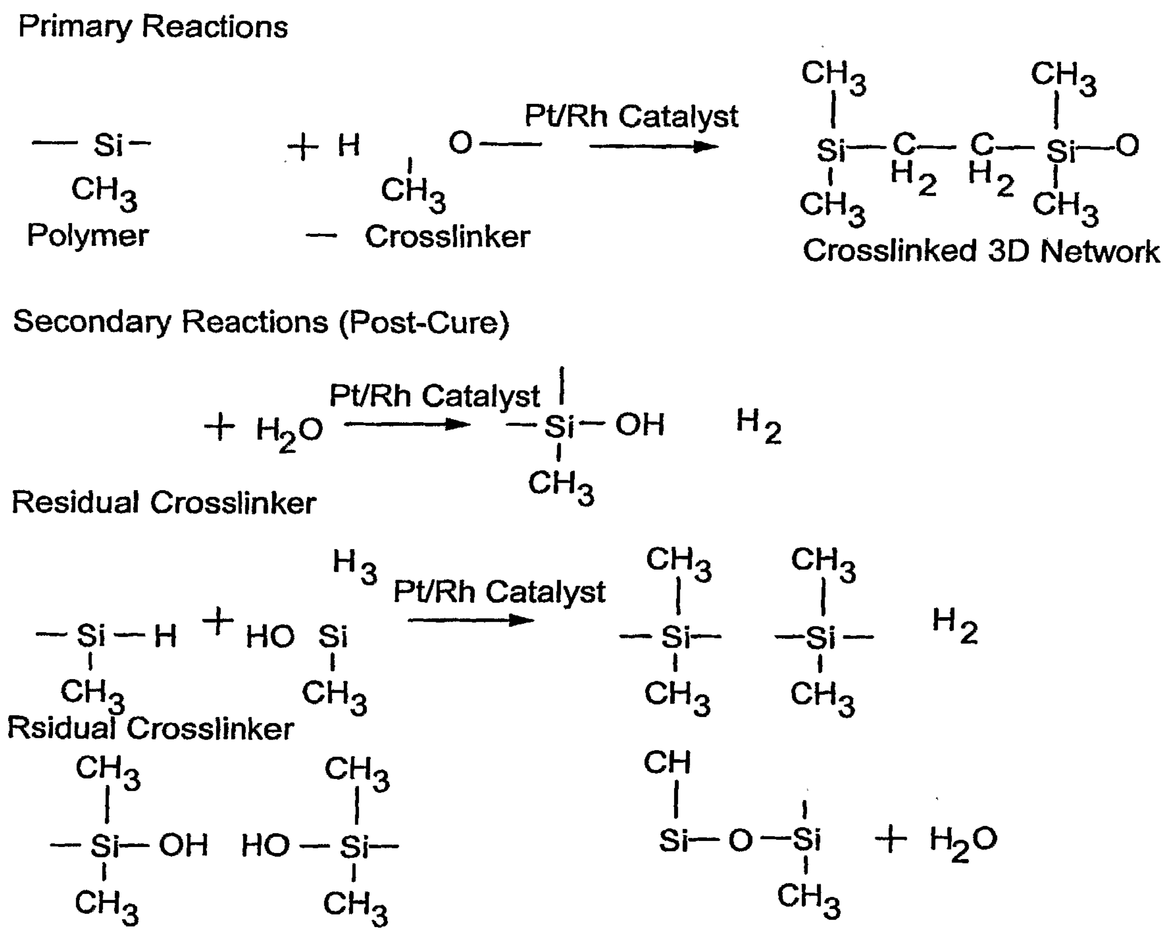
Primary Reactions
Pt/Rh Catalyst
Polymer
Crosslinker
Crosslinked 3D Network
Secondary Reactions (Post-Cure)
Pt/Rh Catalyst
Residual Crosslinker
Pt/Rh Catalyst
Rsidual Crosslinker

Fig. 27